

The Relation Between the Plasticity of a Two Component Solid-Liquid System and the Degree of Wetting of the Solid by the Liquid

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE UNIVERSITY OF MICHIGAN

By
A. Hershberger
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CONTENTS

Introduction.....	5
Method.....	5
Treatment of Results.....	6
Materials.....	7
Experimental.....	9
Systems Falling under Group I.....	10
Systems Falling under Group II.....	18
Method of Preparing Pastes.....	19
Systems Falling under Group III.....	23
Linseed Oil.....	28
Summary.....	31
Bibliography.....	32



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THE RELATION BETWEEN THE PLASTICITY OF A TWO COMPONENT SOLID-LIQUID SYSTEM AND THE DEGREE OF WETTING OF THE SOLID BY THE LIQUID

In much of the work which has been done on plasticity of pastes, linseed oil and similar liquids have been used. Complex reactions may occur between the constituents of these liquids and the dispersed solid phase. In the present investigation reactions of this type were avoided by using pure organic liquids with solids which do not react chemically with them.

Method.—The method used for determining plasticity was, in principle, the same as that used by Moness and Giesy⁸ and by Gregory, Rassweiler, and Lampert.⁴ It consists in measuring the rate of flow of the plastic material through a capillary tube of known dimensions. By using different pressures, different rates of flow are obtained. The results are treated graphically by plotting a function of the time against a function of the pressure. From the curve thus plotted the yield value and the mobility of the material are readily obtained.

The apparatus used is shown in Figure 1. The cell, *A*, is of brass and has a capacity of 15 cc. A calibrated capillary, *B*, is sealed into the end of the screw cap, *C*, with Wood's metal. The other screw cap, *D*, is fitted with a glass tube which passes through a rubber stopper, *E*. The stopper fits the end of the cell and gives an air-tight joint when the cap is screwed down.

To carry out an experiment, the plastometric cell is filled with the paste. Care must be taken to eliminate all air spaces and voids in the paste. The cell is assembled and the caps screwed down tightly. The cell is then connected to the manometer by means of the ground glass joint, *F*. The stopcock, *G*, is closed and the leveling bulb, *H*, raised to the desired height. The stopcock is then opened and the time required for the paste, advancing in the capillary, to pass two etch marks on the tube is noted with a stopwatch. When the stopcock is first opened, the mercury level in the manometer momentarily falls on account of the pressure release. It immediately rises, however, and attains (approximate) constancy before the paste reaches the first etch mark on the capillary. The error due to change in head, caused by the displacement of material from the cell, is less than other experimental errors. As soon as the run is completed the stopcock is again closed and the two levels of mercury read. The cell and capillary are then cleaned and dried, and another run is made using the same material but a different pressure. Six such runs furnish sufficient data for plotting a pressure-flow curve.

Treatment of Results.—In treating the results obtained, the following equation was used:

$$\frac{4\Delta l}{r\Delta t} = \mu \left(\frac{Pr}{2l} - \frac{4}{3}f \right)$$

This equation is a modification of Bingham's equation for representing plastic flow and was first used by Moness and Giesy.⁸ In this equation, l represents the average length of the capillary filled by the material during the time interval of a run. Δl is the distance between the two etch marks on the capillary. The time, Δt , for the material to traverse this distance in the capillary is obtained with a stop-watch. The difference in mercury levels in the manometer gives the pressure, P . The radius of the capillary is represented by r , while μ and f give the mobility and the yield value,

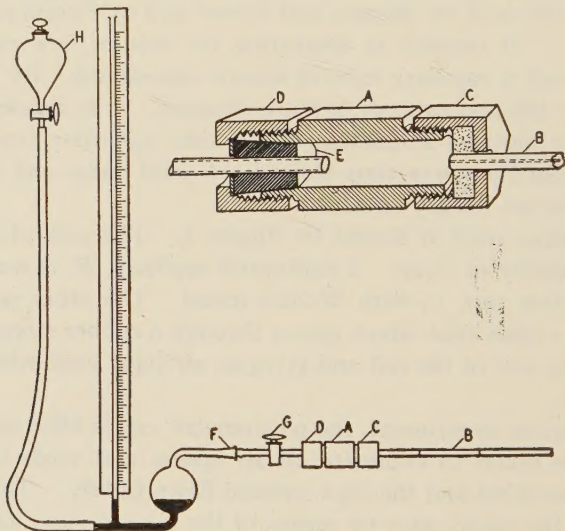


FIGURE 1.—Apparatus Used for Plasticity Measurements.

respectively, of the plastic material. In the present work the same capillary was used throughout. The radius, obtained by weighing a thread of mercury which filled a known length of the capillary, was 0.0911 cm. The distance, Δl , between the etch marks on the capillary was 13.492 cm. The length l was 21.454 cm. Both of these distances were measured with a comparator.

The two variables in the equation are Δt and P . When $4\Delta l/r\Delta t$ is plotted against $Pr/2l$ a curve is obtained which becomes linear for higher values of P . The slope of this linear part gives directly the value of the mobility. By extrapolating the linear part of the curve to the pressure axis an intercept is obtained which has a value equal to $4/3f$. From these

data the yield value (f) of the material is determined. At low pressures the points do not fall in a straight line, but fall to the left, forming a curve. The values for such points have been omitted from the numerical data presented in the present paper.

Materials.—The present work was carried out in an effort to relate the degree of wetting of a given solid by a liquid to the plasticity of a paste

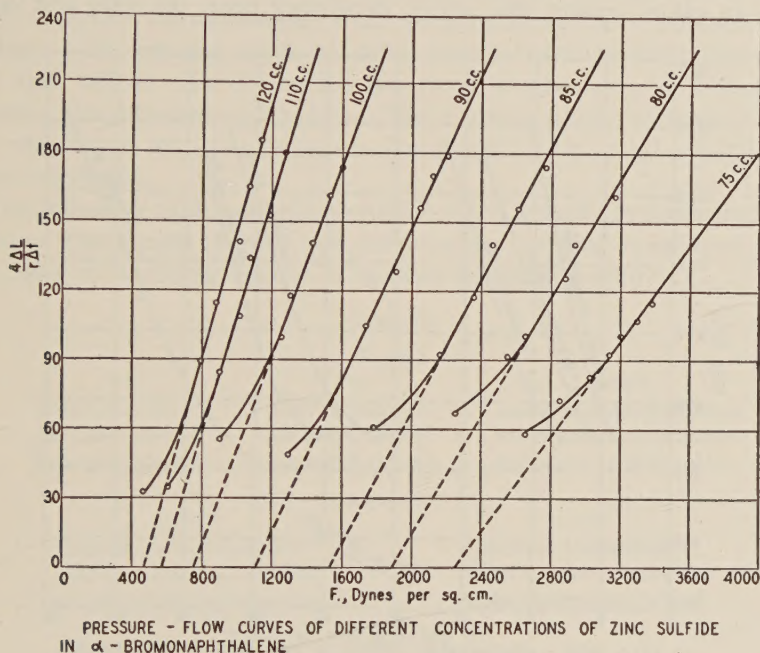


FIGURE 2

formed with this solid and liquid. The degree of wetting of a solid by a liquid is conditioned by the energy change which occurs when a liquid is brought into contact with the solid. An equation derived by Dupré³ which gives this energy change is

$$W_a = S_1 + S_2 - S_{12} \quad (1)$$

where W_a , the work of adhesion, is the work necessary to pull apart 1 cm^2 of solid-liquid interface, S_1 is the surface tension of the solid, S_2 the surface tension of the liquid, and S_{12} the interfacial tension solid-liquid. An equation by Young¹⁰ relating interfacial tensions of such systems with contact angles is as follows:

$$S_1 - S_{12} = S_2 \cos \theta \quad (2)$$

where θ is the angle of contact between the solid and the liquid. Combining the above two equations one obtains

$$W_a = S_2(1 + \cos \theta) = S_2(1 + k) \quad (3)$$

The term k has been called the adhesion constant, and the force of attraction or degree of wetting of a liquid for a solid is directly proportional to its value. In Equation (3) k may have values ranging from less than unity to values greater than unity, depending upon the solid and liquid

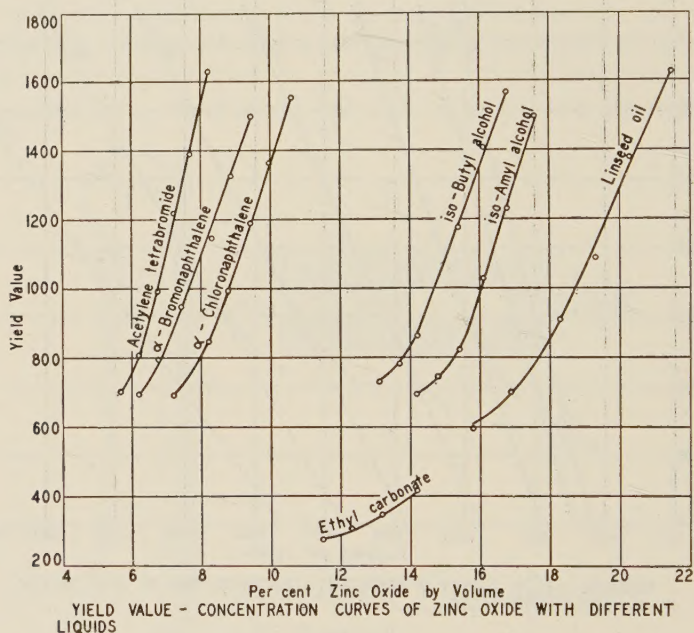


FIGURE 3

used. With a given solid, different liquids fall into one of the three following groups.

Group I $k > 1$

Liquids in this group form zero contact angles with the solid and show a relatively high degree of wetting against the solid.

Group II $k < 1$

Liquids in this group form finite contact angles with the solid and show a relatively low degree of wetting against the solid.

Group III $k \neq 1$

Liquids in this group, although forming zero contact angles with the solid, show an intermediate degree of wetting against the solid. That is,

liquids in this group fall between liquids of Group I and Group II with respect to degree of wetting against a given solid (*i. e.*, values of k approach unity). In the present work liquids and solids were so chosen that each of the three groups was represented.

The solid-liquid systems used which fall under Group I are zinc oxide and zinc sulfide (polar solids) with the liquids, iso-butyl alcohol, iso-amyl alcohol, and ethyl carbonate; and carbon (non-polar solid) with acetylene tetrabromide, α -chloronaphthalene, and α -bromonaphthalene. The systems which fall under Group II are the solids, zinc oxide, and zinc sulfide with the liquids acetylene tetrabromide, α -chloronaphthalene, and α -bromonaphthalene. The systems which fall under Group III are carbon with the liquids iso-butyl alcohol, iso-amyl alcohol, and ethyl carbonate.

The following table contains the solid-liquid systems representing each group. The liquids in each case are arranged in what is believed to be the order of increasing degrees of wetting against the solid.¹

TABLE I

<i>Group I</i>		
ZnO	ZnS	Carbon
Ethyl carbonate	Ethyl carbonate	Alpha-bromonaphthalene
Iso-amyl alcohol	Iso-amyl alcohol	Alpha-chloronaphthalene
Iso-butyl alcohol	Iso-butyl alcohol	Acetylene tetrabromide
<i>Group II</i>		
ZnO	ZnS	
Acetylene tetrabromide	Acetylene tetrabromide	
Alpha-bromonaphthalene	Alpha-bromonaphthalene	
Alpha-chloronaphthalene	Alpha-chloronaphthalene	
<i>Group III</i>		
Carbon		
Iso-butyl alcohol		
Iso-amyl alcohol		
Ethyl carbonate		

Experimental

For each of the above solid-liquid systems a number of pastes were prepared containing different concentrations of solid. The yield values and the mobilities of these pastes were determined. In Tables II to VII, inclusive, Column 1 contains the pressures in centimeters of mercury applied to the paste, while Column 2 contains the time for the material to pass between two etch marks on the capillary. Columns 3 and 4 contain the values obtained for $4\Delta l/r\Delta t$ and $Pr/2l$, respectively. The value $Pr/2l$ multiplied by the density of mercury and the gravitational constant gives the force in dynes per cm^2 applied to the paste. These values plotted against $4\Delta l/r\Delta t$ give the pressure-flow curves. A representative

series of pressure-flow curves of one of the solid-liquid systems used is shown in Figure 2. (This set of curves is in fact but one of the eighteen sets of curves actually obtained, but for economy of space not presented in this paper.) From the intercept of the linear portion of these curves with the pressure axis the yield values were obtained (Tables IX, X, and XI). The mobilities were obtained from the slopes of these curves. Figures 3 to 5 show the yield values for the different solid-liquid systems plotted against volume per cent of solid in the paste, while Figures 6 to 8 show the mobilities of these systems plotted against volume per cent of solid in the paste.

In any solid-liquid system the range of concentrations of solid in liquid used was determined by the yield value-concentration curve. Sufficiently low concentrations of solid were used so that this curve became definitely flexed. It was unnecessary to use lower concentrations than these since in this régime pseudo-plastic flow takes place. Sufficiently high concentrations were used to insure that the linear portion of the curve had been obtained.

Systems Falling under Group I.—The solid-liquid systems falling under Group I will be considered first. It has previously been shown that iso-butyl alcohol gives a higher degree of wetting against the solids ZnO and ZnS than does iso-amyl alcohol. Both liquids, however, give a relatively high degree of wetting against these solids. An examination of the yield value-concentration curves of these systems shows that for equal volumes per cent of solid in these liquids, pastes in which iso-butyl alcohol was used have the higher yield value. The mobility-concentration curves for these same pastes show, however, that the pastes of iso-butyl alcohol have the lower mobility.

If these latter curves be extended to the concentration axis, the intercept will represent the concentration of solid in liquid at which the paste will possess zero mobility. The concentration corresponding to zero mobility for the iso-butyl alcohol pastes is lower than that for the iso-amyl alcohol pastes.

Let us consider a possible explanation for the differences observed between the plastic characteristics of the pastes of these two alcohols. De Waele⁹ has postulated a tightly bound layer of liquid surrounding the solid particles in a paste provided the liquid has a high degree of wetting against the solid constituent of the paste. This view appears logical. Furthermore, it is assumed that the liquid in immediate contact with the tightly bound liquid layer has a much higher viscosity than has the liquid in bulk.⁹

Accepting the above view, we may consider that the molecules of the liquid in immediate contact with the solid are strongly oriented. The liquid molecules in contact with this first layer would also probably tend

to be oriented, though less strongly held. The tendency of the liquid molecules to become definitely oriented would gradually decrease with distance from the solid.

TABLE II

PRESSURE AND TIME INTERVALS OF FLOW OF DIFFERENT SOLID-LIQUID MIXTURES
THROUGH THE CAPILLARY TUBE

40 g ZnO

P (cor.)	t (sec.)	$\frac{4\Delta l}{r\Delta t}$	$\frac{Pr}{2l}$	P (cor.)	t (sec.)	$\frac{4\Delta l}{r\Delta t}$	$\frac{Pr}{2l}$
70 cc alpha-bromonaphthalene				81.5 cc acetylene tetrabromide			
117	4.3	138	.249	120	5.2	113	.256
114	4.7	126	.243	115	5.6	105	.245
107	5.1	115	.228	114	6.0	98	.243
105	5.9	100	.224	109	6.6	89	.232
101	6.4	92	.215	105	7.3	81	.224
75.2 cc alpha-bromonaphthalene				87.5 cc acetylene tetrabromide			
114	3.5	170	.243	117	3.4	174	.249
105	4.1	145	.224	113	3.6	165	.240
101	4.8	123	.215	110	4.1	145	.234
95	5.8	101	.202	100	4.8	123	.213
89	6.2	95	.190	98	5.5	107	.209
80 cc alpha-bromonaphthalene				93.5 cc acetylene tetrabromide			
102	3.2	185	.218	93	3.7	161	.198
95	3.6	165	.202	91	4.4	134	.194
92	4.4	134	.196	85	4.8	123	.181
84	4.9	120	.179	81	5.4	109	.172
80	5.9	100	.170	80	6.5	91	.170
90 cc alpha-bromonaphthalene				100 cc acetylene tetrabromide			
85	3.2	185	.181	85	3.1	190	.181
76	3.7	161	.166	80	3.5	170	.170
74	4.4	134	.157	78	3.9	152	.165
70	5.2	113	.148	73	4.5	131	.155
65	5.9	100	.138	69	5.4	109	.147
100 cc alpha-bromonaphthalene				56	6.5	91	.119
69	3.4	174	.147	110 cc acetylene tetrabromide			
68	3.7	161	.144	73	3.1	190	.155
64	4.2	142	.136	70	3.5	170	.148
59	5.2	113	.125	66	3.9	152	.140
56	6.3	93	.119	62	4.4	134	.132
110 cc alpha-bromonaphthalene				60	5.1	115	.127
63	3.2	185	.134	120 cc acetylene tetrabromide			
60	3.6	165	.127	61	3.6	165	.130
58	4.0	148	.123	58	3.9	152	.123
53	4.8	123	.112	55	4.6	128	.116
49	6.5	91	.104	51	5.5	107	.108
				46	6.7	88	.098

TABLE II (Continued)

PRESSURE AND TIME INTERVALS OF FLOW OF DIFFERENT SOLID-LIQUID MIXTURES
THROUGH THE CAPILLARY TUBE

40 g ZnO

P (cor.)	t (sec.)	$\frac{4 \Delta l}{r \Delta t}$	$\frac{Pr}{2l}$	P (cor.)	t (sec.)	$\frac{4 \Delta l}{r \Delta t}$	$\frac{Pr}{2l}$
61.3 cc alpha-chloronaphthalene				75.3 cc alpha-chloronaphthalene			
119	5.0	118	.253	94	3.2	185	0.200
115	5.4	110	.245	88	3.5	170	.187
110	5.7	103	.234	85	3.9	154	.181
109	6.3	93	.232	79	4.8	123	.168
104	7.0	85	.222	71	5.6	105	.150
97	7.8	76	.206	81.5 cc alpha-chloronaphthalene			
65.5 cc alpha-chloronaphthalene				80	3.2	185	.170
115	3.8	155	.245	75	3.6	165	.159
110	4.1	145	.234	71	4.1	145	.151
105	4.8	123	.225	66	4.9	120	.140
100	5.3	110	.213	60	6.0	98	.127
94	6.4	92	.200	93.7 cc alpha-chloronaphthalene			
87	7.3	81	.185	65	3.4	174	.138
70 cc alpha-chloronaphthalene				61	3.8	156	.129
108	3.3	179	.230	58	4.4	134	.123
102	3.7	161	.217	52	5.4	109	.110
97	4.2	141	.207	46	6.5	91	.098
91	4.8	123	.194				
87	5.6	105	.185				

TABLE III

PRESSURE AND TIME INTERVALS OF FLOW OF DIFFERENT SOLID-LIQUID MIXTURES
THROUGH THE CAPILLARY TUBE

50 g ZnO

P (cor.)	t (sec.)	$\frac{4 \Delta l}{r \Delta t}$	$\frac{Pr}{2l}$	P (cor.)	t (sec.)	$\frac{4 \Delta l}{r \Delta t}$	$\frac{Pr}{2l}$
42.5 cc iso-amyl alcohol				47.5 cc iso-amyl alcohol			
103	3.4	174	0.219	76	3.2	185	0.161
98	3.8	156	.209	73	3.5	170	.155
94	4.4	134	.200	72	3.9	152	.153
92	5.2	113	.195	68	4.2	141	.144
87	5.9	100	.185	66	4.9	120	.140
85	7.9	75	.180	62	5.6	105	.132
45 cc iso-amyl alcohol				59	6.3	93	.125
87	3.2	185	.185	50 cc iso-amyl alcohol			
85	3.7	161	.180	61	3.6	165	.131
80	4.3	138	.170	58	3.9	152	.123
78	4.9	120	.166	56	4.7	126	.119
73	5.8	101	.155	53	5.6	105	.113
71	6.6	89	.151	50	6.3	93	.106

52.5 cc iso-amyl alcohol				45 cc iso-butyl alcohol			
57	3.4	174	0.121	122	6.4	92.0	0.260
55	3.7	161	.116	118	7.2	83.0	.248
51	4.3	138	.108	110	8.6	69.0	.234
50	5.0	118	.106	103	9.6	61.5	.220
47	5.9	100	.100	95	10.2	57.5	.202
46	6.9	86	.098				
55 cc iso-amyl alcohol				47.5 cc iso-butyl alcohol			
54	3.3	179	.115	121	4.5	131	.257
51	3.7	161	.108	115	5.0	118	.245
47	4.7	126	.100	111	5.5	107	.236
46	5.2	113	.098	106	6.1	96	.226
43	6.6	89	.091	100	6.6	89	.213
				95	7.5	79	.202
55 cc ethyl carbonate				50 cc iso-butyl alcohol			
47	3.4	174	.100	114	3.6	165	.243
44	4.0	148	.093	107	3.9	152	.228
39	4.7	126	.083	98	4.7	126	.209
36	5.8	101	.077	93	5.4	109	.198
32	7.5	79	.068	86	6.3	93	.183
				79	7.3	81	.168
60 cc ethyl carbonate				55 cc iso-butyl alcohol			
36	3.1	190	.077	93	3.2	185	.198
33	3.6	165	.070	85	3.9	152	.180
29	4.5	131	.062	79	4.2	141	.168
26	6.2	95	.056	74	4.9	120	.157
				61	7.3	81	.130
65 cc ethyl carbonate				57.5 cc iso-butyl alcohol			
30	3.1	190	.064	82	3.1	190	.174
28	3.4	174	.060	78	3.4	174	.166
27	3.9	152	.058	74	3.8	156	.157
24	4.7	126	.051	67	4.6	128	.142
22	5.7	103	.047	63	5.3	111	.134
				60	5.8	101	.127
70 cc ethyl carbonate				60 cc iso-butyl alcohol			
23	3.3	179	.050	75	3.1	190	.160
21	4.0	148	.045	70	3.5	170	.148
20	4.9	120	.043	66	4.0	147	.140
18	6.4	92	.039	61	4.7	126	.130
				56	5.5	106	.119
				49	6.6	89	.104

There is considerable evidence in support of the view that orientation of liquid molecules extends beyond the surface layer of the liquid. McBain and Davies⁶ conclude from experiments on adsorption that orientation of molecules takes place not only at the surface but extends beneath the surface of the liquid. Hardy⁵ in his study on lubrication states that

"the orientation of molecules at an interface must spread into the overlying fluid until it is destroyed by the heat motions."

In the case of the two alcohols and the solids zinc oxide and zinc sulfide, we shall assume the existence of a stronger tendency toward orientation of the molecules of the iso-butyl alcohol than those of the iso-amyl alcohol. In the former case orientation of the liquid molecules would also extend a greater distance into the liquid medium. It seems probable that this orientation of the liquid molecules between the particles in a paste results in a sort of structure which gives the paste its plastic characteristics.

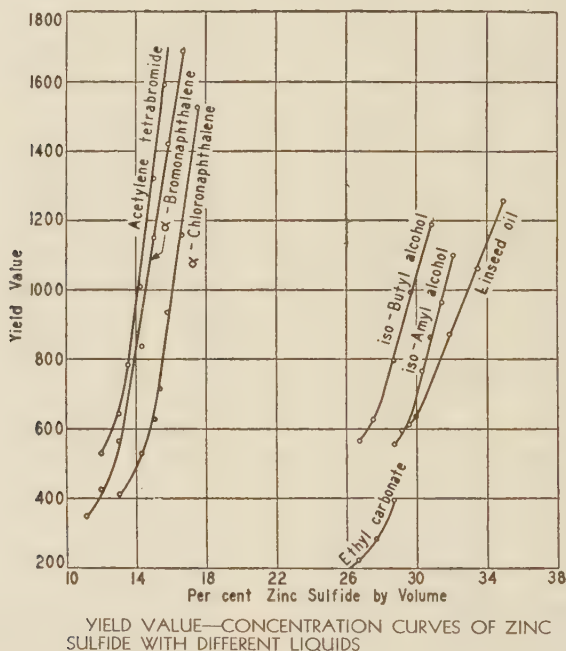


FIGURE 4

The resistance offered by these oriented molecules to deorientation represents the force which resists deformation of the paste. The stronger the orientation tendency of the molecules, the greater will be the force necessary to cause deformation. If the iso-butyl alcohol molecules are in fact the more strongly oriented this would account for the higher yield values of the pastes formed when this liquid is used.

It was noted that the iso-butyl alcohol pastes had lower mobility values than the iso-amyl alcohol pastes at equal concentrations of solid. This cannot be due to the difference in fluidities of the two liquids for iso-butyl

alcohol has the greater fluidity. From the fluidities of the liquids one would expect to obtain results just the reverse of those found.

The mobilities of the two pastes then offer further evidence that the molecules of the better wetting liquid are the more strongly oriented and the more firmly held. The more strongly oriented iso-butyl alcohol molecules will tend to give the liquid surrounding the solid particles a greater viscosity which in turn would lower the mobility of this paste. The molecules which are deoriented during flow will tend to reorient themselves. The greater this tendency to reorient, the greater the con-

TABLE IV
PRESSURE AND TIME INTERVALS OF FLOW OF DIFFERENT SOLID-LIQUID MIXTURES
THROUGH THE CAPILLARY TUBE

60 g ZnO							
P (cor.)	t (sec.)	$\frac{4\Delta l}{r\Delta t}$	$\frac{Pr}{2l}$	P (cor.)	t (sec.)	$\frac{4\Delta l}{r\Delta t}$	$\frac{Pr}{2l}$
39.7 cc linseed oil				48.7 cc linseed oil			
118	3.6	165	.251	78	3.2	185	.166
114	4.0	148	.243	75	3.5	170	.159
110	4.5	131	.234	69	4.4	134	.147
106	5.1	115	.225	65	5.1	115	.138
101	5.9	100	.215	62	6.0	98	.132
97	6.9	86	.206	57	7.2	83	.121
42.7 cc linseed oil				53.7 cc linseed oil			
108	3.3	179	.230	61	3.5	170	.130
103	3.7	161	.220	58	4.1	145	.123
99	4.2	141	.211	54	4.7	126	.115
95	4.8	123	.202	50	5.8	101	.106
91	5.6	105	.194	46	7.6	78	.097
96	6.3	93	.183	57.8 cc linseed oil			
45.7 cc linseed oil				52	3.5	170	.110
90	3.4	174	.191	48	4.1	145	.102
85	4.0	148	.180	47	4.6	128	.100
79	4.7	126	.168	44	5.3	111	.093
75	5.7	103	.159	42	6.5	91	.089
68	6.9	86	.144				

stant force which would have to be applied to maintain a constant velocity of flow.

It was observed further that the concentration representing zero mobility for the pastes in which iso-butyl alcohol was used, was lower than for pastes in which iso-amyl alcohol was used. In a paste approaching the concentration of zero mobility the solid particles are brought quite closely together; orientation of the liquid molecules may extend through the entire distance between the particles. This would tend to cause the paste to become immobile. In the case of iso-butyl alcohol pastes this

condition is likely to be reached at a lower concentration of solid than in the iso-amyl alcohol pastes. In the ormer paste the force of attraction solid-liquid is the greater, therefore the tendency toward orientation of the liquid molecules is greater, and consequently oriented molecules will extend farther into the surrounding liquid.

It would have been desirable to have determined the plasticities of pastes formed with a larger number of liquids having relatively high degrees of wetting for the solid. Ethyl carbonate was tried; this liquid gives a somewhat lower degree of wetting with ZnO and ZnS than do either of the two alcohols. The pastes prepared by using this liquid, however, give poor results. Only relatively low concentrations of solid could be used with this liquid. At the higher concentrations extensive seepage took place. This probably was due to the lower force of attraction between the solids and this liquid.

TABLE V
PRESSURE AND TIME INTERVALS OF FLOW OF DIFFERENT SOLID-LIQUID MIXTURES
THROUGH THE CAPILLARY TUBE

60 g ZnS							
<i>P</i> (cor.)	<i>t</i> (sec.)	$\frac{4 \Delta l}{r \Delta t}$	$\frac{Pr}{2l}$	<i>P</i> (cor.)	<i>t</i> (sec.)	$\frac{4 \Delta l}{r \Delta t}$	$\frac{Pr}{2l}$
75 cc alpha-bromonaphthalene				100 cc alpha-bromonaphthalene			
120	5.1	115	0.256	57	3.4	174	0.121
117	5.5	107	.249	54	3.7	161	.115
113	5.8	101	.241	51	4.2	141	.108
111	6.4	92	.237	46	5.0	118	.098
107	7.2	83	.228	44	5.9	100	.094
101	8.1	73	.215	110 cc alpha-bromonaphthalene			
80 cc alpha-bromonaphthalene				45	3.3	179	.096
112	3.7	161	.239	42	3.9	152	.089
104	4.2	141	.222	38	4.4	134	.081
102	4.7	126	.218	36	5.4	109	.076
99	5.2	113	.211	32	7.0	85	.068
94	5.8	101	.200	120 cc alpha-bromonaphthalene			
90	6.4	92	.192	40	3.2	185	.085
85 cc alpha-bromonaphthalene				38	3.6	165	.081
98	3.4	174	.209	36	4.2	141	.076
93	3.8	156	.197	31	5.1	115	.066
87	4.2	141	.185	28	6.6	89	.060
84	5.0	118	.178	70.6 cc alpha-chloronaphthalene			
77	6.3	93	.163	119	4.3	138	.253
90 cc alpha-bromonaphthalene				113	4.7	125	.241
78	3.3	179	.166	109	5.5	107	.232
75	3.5	170	.160	104	6.1	96	.222
73	3.8	156	.155	100	7.1	84	.213
68	4.6	128	.144	94	8.0	74	.200
60	5.6	105	.127				

75 cc alpha-chloronaphthalene				80 cc acetylene tetrabromide			
105	3.3	179	0.224	112	7.0	85	0.239
100	3.6	165	.213	106	7.8	76	.226
97	4.2	141	.207	103	9.2	64	.220
91	4.5	131	.194	98	10.5	56	.209
87	5.2	113	.185	95	12.9	46	.202
83	5.7	103	.176	91	13.9	43	.194
80 cc alpha-chloronaphthalene				85 cc acetylene tetrabromide			
86	3.3	179	.183	108	4.0	148	.230
80	3.8	156	.170	100	4.5	131	.213
78	4.3	138	.165	97	5.2	113	.207
73	4.8	123	.155	92	5.8	101	.196
69	5.3	111	.146	88	6.8	87	.187
64	6.5	91	.136	81	8.0	74	.172
82.5 cc alpha-chloronaphthalene				90 cc acetylene tetrabromide			
70	3.3	179	.149	85	3.9	152	.181
65	3.7	161	.137	81	4.5	131	.172
62	4.3	138	.132	76	5.1	115	.161
59	4.7	126	.125	72	6.1	96	.153
55	5.5	107	.116	66	7.6	78	.140
85 cc alpha-chloronaphthalene				95 cc acetylene tetrabromide			
65	3.2	185	.138	74	3.6	165	.157
60	3.7	161	.127	69	4.1	145	.147
55	4.3	138	.117	66	4.6	128	.140
51	5.2	113	.108	62	5.3	111	.132
48	6.2	95	.102	57	6.0	98	.121
90 cc alpha-chloronaphthalene				54	7.3	81	.115
56	3.3	179	.119	100 cc acetylene tetrabromide			
50	4.1	145	.106	64	3.5	170	.135
46	4.7	126	.097	59	3.9	152	.125
43	5.9	100	.091	56	4.5	131	.118
38	7.2	83	.081	53	5.2	113	.113
77 cc acetylene tetrabromide				48	6.2	95	.102
120	9.0	66	.256	110 cc acetylene tetrabromide			
117	9.4	63	.249	51	3.5	170	.108
115	10.5	56	.245	50	3.9	154	.106
112	11.1	53	.239	45	4.6	128	.096
108	11.8	50	.230	42	5.3	111	.089
				41	6.2	95	.087
				36	7.1	84	.077

The pastes formed by carbon with the liquids acetylene tetrabromide, α -chloronaphthalene, and α -bromonaphthalene gave systems which also fall under Group I. The behavior of these pastes were very similar to those of ZnO and ZnS with the two alcohols as described above. Thus with equal volumes per cent of carbon in the liquids the yield value of the acetylene tetrabromide paste was the greatest, that of α -chloro-

naphthalene lower, and that of α -bromonaphthalene the lowest. The mobilities of these pastes increase in the opposite order. The concentration corresponding to zero mobility is lowest for the acetylene tetrabromide paste and highest for the α -bromonaphthalene pastes.

Reference to Table I shows that in the case of carbon pastes also, for equal volumes per cent of solid, the highest yield values were obtained with the pastes in which the best wetting liquid was used. Again also, lowest mobility of paste was obtained with the best wetting liquid. An explanation for the behavior of the carbon pastes is the same as that for the zinc oxide and zinc sulfide pastes. It is postulated that the liquid

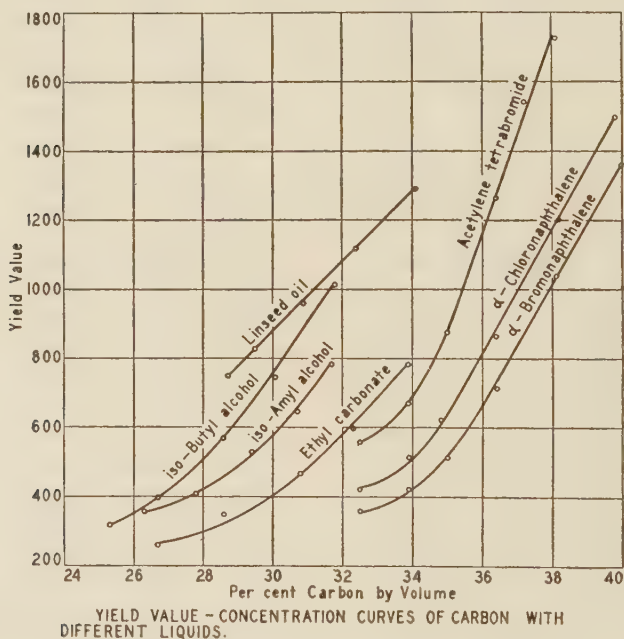


FIGURE 5

giving the highest degree of wetting gives the highest degree of molecular orientation toward the solid phase and that resistance to deorientation results in a high yield value and low mobility. The zero mobility value for the best wetting liquid is, in this case also, obtained with a paste with lower concentration of solid than is necessary for the pastes formed with the poorer wetting liquids.

These facts indicate that the interfacial energy relationships between solid and liquid must be predominating factors in determining the characteristics of the pastes.

Systems Falling under Group II.—The solid-liquid systems falling

under Group II are ZnO and ZnS with the three liquids, acetylene tetrabromide, α -bromonaphthalene, and α -chloronaphthalene. These liquids form finite contact angles with the solids and hence wet them poorly.

Method of Preparing Pastes.—It was found necessary to use a different procedure in making up the pastes when liquids of Group II were used. When preparing pastes with the high degree of wetting liquids, such as were used in Group I, the liquid was added to the solid and thoroughly stirred by means of a glass rod. Since the liquid spontaneously wetted the solid, a uniform paste was obtained in this simple manner. Just before each run the paste was again stirred to eliminate settling. Table VIII shows the times of flow of such a paste of ZnO and iso-butyl alcohol using a constant head of pressure. With such paste the times of flow remained constant.

In the same table are shown the times of flow of a paste of ZnO and acetylene tetrabromide, which falls in Group II. This paste was made up in precisely the same manner as were the iso-butyl alcohol-ZnO paste. The figures show that successive recorded times of flow of the contact angle liquid pastes decrease with a given pressure head in a more or less uniform manner. This change may be due to a more complete wetting of the powder by the liquid in each of the successive runs since the pastes were thoroughly stirred before each run. Bingham and Jacques² observed that with continued grinding of a paint both the mobility and the yield value decreased. This was probably due to an increasingly more thorough mixing of the pigment with the vehicle.

Obviously, in the present work, it was necessary to stir the solids with these contact angle liquids for some time in order to insure complete wetting. To accomplish this the paste was first mixed with a stirring rod and then placed in a small ball mill. The mill was rotated rather slowly for two hours. This procedure tended to mix the paste but did not disintegrate the individual pigment particles. The paste was then removed and the times of flow at constant pressure head determined. These times of flow were constant as shown in Table VIII. All of the pastes made with the liquids in Group II were treated in this manner before the plasticity was determined.

In comparing the yield value-concentration curves of the systems belonging to Group II, it is observed that for equal volumes per cent of solids, zinc oxide, and zinc sulfide, in these three liquids, the yield values of the pastes decrease in the order acetylene tetrabromide, α -bromonaphthalene, and α -chloronaphthalene. The mobility-concentration curve show that at equal volumes per cent of solid in these three liquids the mobilities increase in the order given above. The intercepts on the concentration axis obtained by extending these latter curves give the concentrations representing zero mobility for the three solid-liquid systems.

The concentration representing zero mobility is lowest for the system in which acetylene tetrabromide is used and highest for the system in which α -chloronaphthalene is used.

Reference to Table I shows that the order of increasing degrees of wetting of these three liquids for the solids (ZnO and ZnS) is acetylene tetrabromide, α -bromonaphthalene, and α -chloronaphthalene. The experimental data shows that for equal concentrations of solid in these

TABLE VI
PRESSURE AND TIME INTERVALS OF FLOW OF DIFFERENT SOLID-LIQUID MIXTURES
THROUGH THE CAPILLARY TUBE

<i>80 g ZnS</i>							
<i>P</i> (cor.)	<i>t</i> (sec.)	$\frac{4 \Delta l}{r \Delta t}$	$\frac{Pr}{2l}$	<i>P</i> (cor.)	<i>t</i> (sec.)	$\frac{4 \Delta l}{r \Delta t}$	$\frac{Pr}{2l}$
37 cc linseed oil				49.8 cc ethyl carbonate			
118	5.1	115	.251	60	3.8	156	.127
113	5.4	109	.241	53	4.1	145	.113
110	5.9	100	.234	51	4.6	128	.108
105	6.3	93	.224	46	5.2	113	.097
101	6.7	88	.215	43	6.3	93	.092
96	7.2	83	.204	38	7.3	81	.081
39.6 cc linseed oil				52.4 cc ethyl carbonate			
117	3.6	165	.249	49	3.3	179	.104
113	3.9	152	.241	48	3.5	170	.102
104	4.4	137	.222	46	3.8	156	.097
98	5.2	113	.209	41	4.7	126	.087
89	6.0	98	.190	33	5.6	105	.070
83	6.6	89	.176	27	8.6	69	.058
42.7 cc linseed oil				55 cc ethyl carbonate			
91	3.5	170	.193	41	3.2	185	.087
85	4.0	148	.180	40	3.5	171	.085
76	4.8	123	.161	35	3.7	161	.075
69	6.2	95	.147	33	4.3	138	.071
63	7.6	78	.134	30	4.8	123	.064
46.7 cc linseed oil				29	5.3	111	.062
67	3.5	170	.142	60 cc ethyl carbonate			
60	4.2	141	.127	34	3.2	185	.072
56	4.8	123	.119	29	3.8	156	.062
51	5.9	100	.108	26	4.4	134	.055
47	7.3	81	.100	24	5.2	113	.051
48.6 cc linseed oil				19	6.9	86	.041
60	3.3	179	.127	42.3 cc iso-amyl alcohol			
57	3.8	156	.121	119	4.8	123	.253
51	4.7	126	.108	113	5.2	113	.240
47	5.9	100	.100	109	5.7	103	.232
39	7.8	76	.083	104	6.1	96	.221
				99	6.3	93	.211

43.5 cc iso-amyl alcohol				44.9 cc iso-butyl alcohol			
112	3.8	156	0.239	118	5.1	115	0.251
102	4.4	134	.217	113	5.6	105	.240
96	5.1	115	.204	108	6.3	93	.230
88	6.0	98	.187	101	7.1	84	.215
80	7.0	85	.170	93	8.0	74	.198
45 cc iso-amyl alcohol				47.4 cc iso-butyl alcohol			
97	3.4	174	.207	102	3.5	170	.217
91	3.8	156	.193	94	4.1	145	.200
85	4.3	138	.180	93	4.7	126	.198
77	5.2	113	.164	81	5.7	103	.172
70	6.4	92	.148	74	6.9	86	.157
46 cc iso-amyl alcohol				49.8 cc iso-butyl alcohol			
86	3.3	179	.183	75	3.3	179	.159
81	3.7	161	.172	70	3.9	152	.148
73	4.4	134	.155	64	4.8	123	.136
67	5.4	109	.142	59	5.6	105	.125
57	7.6	78	.121	56	7.0	85	.119
47.6 cc iso-amyl alcohol				50	8.5	70	.106
69	3.2	185	.147	52.4 cc iso-butyl alcohol			
65	3.7	161	.138	59	3.2	185	.125
59	4.4	134	.125	55	3.6	165	.117
54	5.2	113	.115	51	4.3	138	.108
50	6.5	91	.106	47	5.0	118	.100
44	8.4	71	.094	45	6.1	96	.095
49.8 cc iso-amyl alcohol				40	7.2	83	.085
57	3.4	174	.121	54.9 cc iso-butyl alcohol			
51	4.1	145	.109	46	3.6	165	.098
48	5.0	118	.102	44	4.2	141	.094
43	6.1	96	.091	40	5.1	115	.086
35	5.9	59	.074	37	7.0	85	.079
				33	8.1	73	.070

liquids the paste in which the poorest wetting liquid is used has the highest yield value and the lowest mobility; also that the system in which the poorest wetting liquid is used has the lowest concentration for zero mobility.

The behavior of the solid-liquid systems in Group II observed above appears to be due to the fact that all of these liquids wet the solids poorly. In systems which belong to this group the work of cohesion of the liquid for itself is greater than the work of adhesion solid-liquid. That is, the liquid molecules have a greater attraction for each other than they have for the solid particles dispersed in the liquid. Hence an attraction between the dispersed particles results. This, according to de Waele, leads to flocculation or grouping of the solid particles into clusters in the liquid medium.

In such a flocculated system the solid particles are in actual contact with each other. It is this flocculated structure which gives the paste its plastic characteristics. When such a system is sheared the resistance offered by the paste to deformation is due to friction between the actual points of contact of the solid particles. This factor, then, determines the yield value of the paste. The more poorly the liquid wets the solid the greater is the tendency toward flocculation. This leads to relatively more points of contact between the solid particles. A paste with a liquid which poorly wets the solid would consequently have a greater yield value than would a paste in which the liquid had a somewhat higher degree of

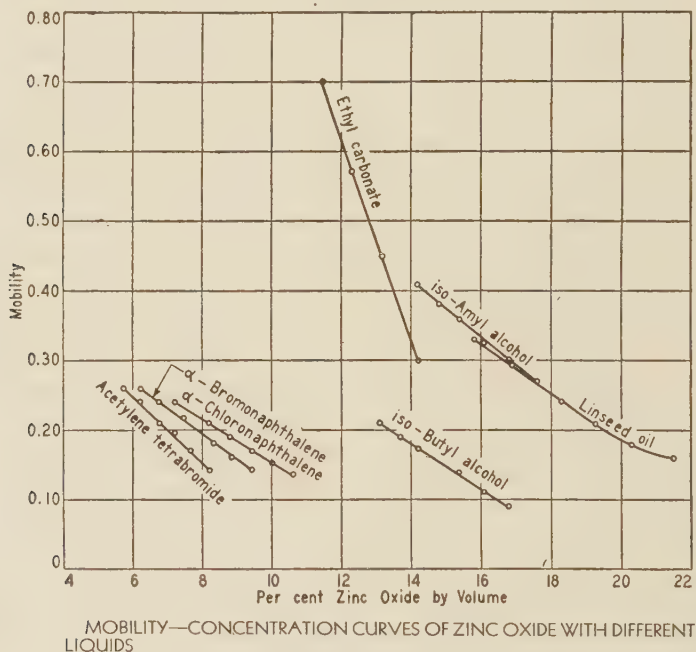
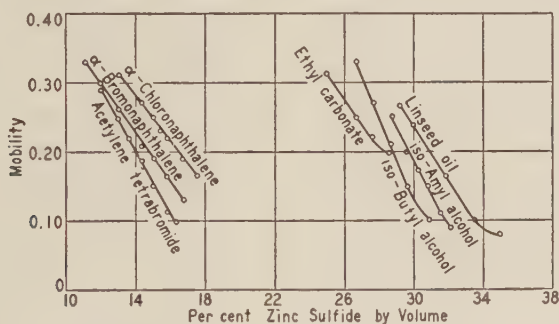


FIGURE 6

wetting with the solid. This is in accord with the experimental results. For equal volumes per cent of solid in the liquids used, the paste in which the poorest wetting liquid was used had the highest yield value.

After the yield value of such a system is reached, and flow is taking place, the tendency for reflocculation to occur is still present. The greater this tendency the greater will be the force necessary to maintain a constant rate of flow. Consequently such a paste would have a low mobility. It was found experimentally that for equal volumes per cent of solid in the three poorly wetting liquids the paste in which the poorest wetting liquid was used had the lowest mobility.

The concentration of solid representing "zero mobility" of the systems has been found to depend upon the degree of wetting of the solid by the liquid. The solid-liquid system in which the poorest wetting liquid is used is flocculated to the greatest extent. As previously pointed out this results in a greater number of points of contact between the solid particles. As the concentration of solid in the liquid is increased the number of points of contact between the solid particles is increased until the paste has zero mobility. The above may account for the fact that the system in which the poorest wetting liquid was used had the lowest concentration at zero mobility. The results are also in harmony with the fact that has been noted in the previous work that the interfacial tension relationships of polar solids against a series of liquids are practically opposite to those of non-polar solids, as carbon, against the same series of liquids.



MOBILITY-CONCENTRATION CURVES OF ZINC SULFIDE
WITH DIFFERENT LIQUIDS

FIGURE 7

Systems Falling under Group III.—As previously pointed out the solid-liquid systems placed in this group only approximate the condition $k = 1$; in fact k was somewhat greater than unity, though in some cases probably approached this value. The force of attraction between the solid and these liquids has an intermediate value between the forces of attraction existing between solid and liquid in the systems in Group I and Group II. The liquids placed in this group form zero contact angles with carbon and consequently spontaneously wet it. In this respect the systems are similar to the systems in Group I. On the other hand flocculation of the carbon particles does take place to a limited extent in these liquids. In this respect the systems are similar to the systems in Group II. The plastic characteristics of pastes in this group would then be expected to be due to a combination of influences, namely: the orientation of liquid molecules resulting from the force of attraction solid-liquid; and the friction existing between the solid particles resulting from flocculation.

TABLE VII

PRESSURE AND TIME INTERVALS OF FLOW OF DIFFERENT SOLID-LIQUID MIXTURES
THROUGH THE CAPILLARY TUBE

<i>40 g Carbon</i>							
<i>P</i> (cor.)	<i>t</i> (sec.)	$\frac{4 \Delta l}{r \Delta t}$	$\frac{Pr}{2l}$	<i>P</i> (cor.)	<i>t</i> (sec.)	$\frac{4 \Delta l}{r \Delta t}$	$\frac{Pr}{2l}$
39 cc ethyl carbonate				44.7 cc linseed oil			
93	3.3	179	.198	61	3.2	185	.130
85	3.7	161	.181	60	3.5	170	.127
80	4.3	138	.170	58	4.2	141	.123
70	5.3	111	.149	56	5.1	115	.119
65	7.0	85	.138	54	6.6	89	.115
42 cc ethyl carbonate				47.7 cc linseed oil			
72	3.2	185	.153	52	3.2	185	.110
65	3.6	165	.138	51	3.5	170	.108
60	4.4	134	.127	50	4.0	148	.106
53	5.4	109	.112	48	4.6	128	.102
47	7.7	77	.100	45	6.1	97	.095
45 cc ethyl carbonate				43	8.5	70	.091
58	3.1	190	.123	49.7 cc linseed oil			
54	3.6	165	.115	43	3.6	165	.091
48	4.3	138	.102	42	4.1	145	.089
43	5.5	107	.091	39	4.9	120	.083
34	8.4	71	.072	38	6.4	92	.081
50 cc ethyl carbonate				35	9.6	61	.075
41	3.2	185	.087	30 cc alpha-bromonaphthalene			
36	3.8	156	.077	90	3.4	174	.191
33	4.7	126	.070	85	3.9	152	.181
28	6.1	96	.060	84	4.5	131	.178
25	8.8	67	.053	80	5.2	113	.170
55 cc ethyl carbonate				78	6.2	95	.165
31	3.3	179	.066	75	7.3	81	.160
27	3.8	156	.058	32.5 cc alpha-bromonaphthalene			
26	4.6	128	.055	69	3.2	185	.147
21	6.3	93	.045	67	3.7	161	.142
18	10.1	58	.038	65	4.3	138	.137
38.7 cc linseed oil				62	5.0	118	.132
94	3.3	179	.200	60	6.3	93	.127
89	4.0	148	.189	35 cc alpha-bromonaphthalene			
85	4.8	123	.180	50	3.1	190	.106
79	5.8	101	.168	47	3.6	165	.100
75	7.6	78	.159	46	4.2	141	.098
41.7 cc linseed oil				43	5.0	118	.091
73	3.3	179	.155	42	6.4	92	.089
70	3.9	152	.148	37 cc alpha-bromonaphthalene			
68	4.6	128	.144	39	3.2	185	.083
64	6.0	98	.136	37	3.7	161	.079
61	9.1	65	.130				

35	4.5	131	0.074
31	5.8	101	.066
30	7.7	77	.064

39 cc alpha-bromonaphthalene

34	3.2	185	.073
32	3.8	156	.068
30	4.6	127	.064
28	6.0	98	.060
26	8.2	72	.055

41.5 cc alpha-bromonaphthalene

29	3.2	185	.062
26	3.7	161	.056
25	4.5	131	.053
23	5.9	100	.049
21	7.7	77	.045

43 cc iso-amyl alcohol

105	3.7	161	.224
97	4.1	145	.206
89	4.8	123	.190
80	5.8	101	.170
71	7.0	85	.150

45 cc iso-amyl alcohol

92	3.2	185	.196
87	3.4	174	.185
79	4.0	148	.168
70	4.8	123	.148
61	6.3	93	.130
51	8.2	72	.108

48 cc iso-amyl alcohol

66	3.1	190	.140
63	3.3	179	.134
57	3.9	152	.121
53	4.6	128	.112
45	6.0	98	.096
40	7.8	76	.085

52 cc iso-amyl alcohol

47	3.2	185	.100
45	3.5	170	.095
41	4.0	148	.087
36	5.3	111	.077
30	7.9	75	.064
27	9.9	59	.058

56 cc iso-amyl alcohol

38	3.1	190	.081
34	3.6	165	.073
31	4.3	138	.066
29	5.4	109	.062
25	7.3	81	.053

32 cc acetylene tetrabromide

123	5.2	113	0.262
117	6.1	96	.249
112	7.5	79	.239
108	8.8	67	.230
102	10.6	55	.217

32.5 cc acetylene tetrabromide

119	4.0	148	.253
113	4.9	120	.240
108	5.7	103	.230
101	8.1	73	.215
93	11.3	52	.198

33.7 cc acetylene tetrabromide

108	3.4	174	.230
102	3.8	156	.217
98	4.6	128	.209
94	5.3	111	.200
89	7.2	83	.190

35 cc acetylene tetrabromide

85	3.4	174	.181
80	4.0	148	.170
78	4.7	126	.166
74	6.0	98	.157
71	8.1	73	.151
66	9.8	60	.140

37 cc acetylene tetrabromide

61	3.3	179	.129
57	3.8	156	.121
55	4.5	131	.117
54	5.5	107	.114
48	7.7	77	.102

39 cc acetylene tetrabromide

50	3.2	185	.106
47	3.7	161	.100
44	4.6	128	.094
41	5.8	101	.087
39	7.1	84	.083

41.5 cc acetylene tetrabromide

40	3.2	185	.085
38	3.6	165	.081
36	4.5	131	.077
33	5.6	105	.070

30.2 cc alpha-chloronaphthalene

102	3.5	170	.218
97	4.0	148	.207
94	4.8	123	.200
89	6.0	98	.189
84	7.5	79	.178

TABLE VII (Continued)

PRESSURE AND TIME INTERVALS OF FLOW OF DIFFERENT SOLID-LIQUID MIXTURES
THROUGH THE CAPILLARY TUBE

40 g Carbon

P (cor.)	t (sec.)	$\frac{4\Delta l}{r\Delta t}$	$\frac{Pr}{2l}$	P (cor.)	t (sec.)	$\frac{4\Delta l}{r\Delta t}$	$\frac{Pr}{2l}$
32.5 cc alpha-chloronaphthalene				43 cc iso-butyl alcohol			
80	3.4	174	.170	101	3.3	179	.215
77	3.8	156	.164	94	3.8	156	.200
75	4.5	131	.160	90	4.2	141	.191
71	5.7	103	.150	85	4.8	123	.180
68	7.5	79	.144	77	6.0	98	.164
63	9.6	61	.134	69	7.9	75	.147
35 cc alpha-chloronaphthalene				46.5 cc iso-butyl alcohol			
60	3.3	179	.127	71	3.6	165	.151
56	3.9	152	.119	67	4.4	134	.142
54	4.6	128	.115	61	5.0	118	.130
51	5.7	105	.108	56	6.5	91	.119
47	8.7	68	.100	48	9.1	65	.102
37.5 cc alpha-chloronaphthalene				50 cc iso-butyl alcohol			
44	3.3	179	.094	54	3.2	185	.115
43	3.7	161	.092	49	3.9	152	.104
40	4.4	134	.085	46	4.6	128	.098
38	6.0	98	.081	42	5.4	109	.089
35	8.1	73	.075	39	7.0	85	.083
39 cc alpha-chloronaphthalene				55 cc iso-butyl alcohol			
37	3.4	174	.078	40	3.2	185	.085
36	3.9	152	.076	35	3.9	152	.074
33	4.8	123	.070	33	4.7	126	.070
31	6.4	92	.066	29	5.9	100	.062
29	8.8	67	.062	26	7.7	77	.056
41.5 cc alpha-chloronaphthalene				59 cc iso-butyl alcohol			
32	3.4	174	.068	31	3.4	174	.066
30	3.7	161	.064	29	3.8	156	.062
29	4.4	134	.062	28	4.4	134	.060
26	6.2	95	.055	24	6.1	96	.051
23	10.8	54	.050	20	8.8	67	.043

The yield value-concentration curves show that for equal volumes per cent of solid in the liquids of this group the order of increasing yield values is ethyl carbonate, iso-amyl alcohol, and iso-butyl alcohol. Reference to Table I shows that this is the order of decreasing degrees of wetting of these liquids for carbon. Thus the paste with the liquid which wets the solid the poorest has the highest yield value. This is the same condition that was found to exist in the systems in Group II. It can be reasoned then that the pastes in Group III likewise owe their plastic

characteristics to the friction between the solid particles as a result of flocculation tendencies.

TABLE VIII

EFFECT OF STIRRING ON THE TIME INTERVALS OF FLOW OF DIFFERENT PASTES AT A CONSTANT PRESSURE

ZnO + acetylene tetrabromide— without stirring	ZnO + acetylene tetrabromide— after 2 hours' stirring	Iso-butyl alcohol + ZnO—without stirring
8.8 sec.	7.4 sec.	8.4 sec.
8.1 "	7.3 "	8.4 "
7.6 "	7.3 "	8.3 "
6.9 "	7.4 "	8.4 "
6.8 "	7.3 "	8.4 "
6.5 "	7.4 "	8.3 "
6.3 "		
6.4 "		

TABLE IX

THE RELATION BETWEEN THE VOLUMES PER CENT OF A SOLID IN A LIQUID AND THE TWO PROPERTIES, YIELD VALUE AND MOBILITY

ZnO					
Vol. %	<i>f</i>	μ	Vol. %	<i>f</i>	μ
Alpha-bromonaphthalene			Alpha-chloronaphthalene		
6.2	696	0.26	7.2	690	0.24
6.77	795	.24	8.2	848	.21
7.48	945	.218	8.8	994	.19
8.34	1142	.18	9.42	1190	.17
8.85	1325	.165	10.0	1365	.15
9.42	1500	.143	10.6	1550	.135
Acetylene tetrabromide			Iso-butyl alcohol		
5.7	702	.26	13.1	729	.21
6.2	809	.24	13.7	782	.19
6.77	994	.21	14.2	861	.173
7.2	1220	.195	15.4	1175	.14
7.68	1390	.17	16.1	1405	.112
8.2	1630	.14	16.8	1564	.09
Iso-amyl alcohol			Linseed oil		
14.2	696	.41	15.8	596	.33
14.8	743	.38	16.9	700	.292
15.4	820	.36	18.3	903	.24
16.1	1030	.325	19.3	1085	.21
16.8	1230	.30	20.3	1380	.18
17.6	1500	.27	21.5	1630	.16
Ethyl carbonate					
11.5	278	.70			
12.3	308	.57			
13.2	347	.45			
14.2	418	.30			

Comparison of the mobilities of equal volumes per cent of solid in the liquids taken from the mobility-concentration curves, do not show a uniform relationship between degree of wetting of the liquids for carbon and the mobility of the pastes. The paste in which ethyl carbonate is used has the highest mobility; this is similar to the results found in the systems used in Group II. That is, the paste in which the best wetting liquid is used has the highest mobility. However, the pastes in which the two alcohols were used have this order reversed. In general, it would appear that the plastic characteristics are a result of the flocculation tendency. It should be noted that the order of mobilities of these pastes in this group is the same as the order of the fluidities of the liquid m

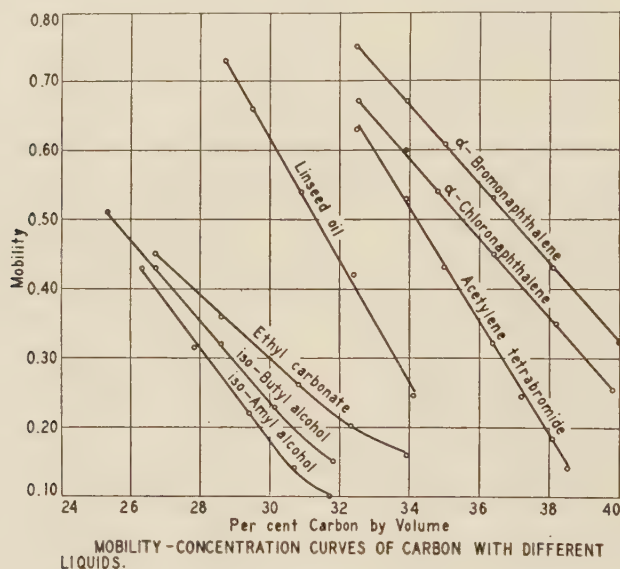


FIGURE 8

used. This would seem to indicate that the flocculation tendencies of the two alcohols are quite nearly alike, the work of adhesion is low and consequently the fluidities of the liquids have the more important effect upon the mobilities of the pastes.

From the mobilities and yield values of the pastes using liquids in Group III it would appear that the flocculation tendency is an important factor in producing the plastic characteristics of these pastes. This tendency, however, is not so predominant as it is in the case of the systems in Group II.

Linseed Oil.—Inasmuch as linseed oil serves as the liquid medium in the preparation of technical pastes such as are employed in the paint

and varnish industry, it appeared that it would be of some importance to know to which of the three groups discussed above linseed oil belongs. McMillen⁷ determined the degree of wetting of lithopone against several pure synthetic linseed oil derivatives by means of adhesion tension measure-

TABLE X

THE RELATION BETWEEN THE VOLUMES PER CENT OF A SOLID IN A LIQUID AND THE TWO PROPERTIES, YIELD VALUE AND MOBILITY

<i>ZnS</i>					
Vol. %	<i>f</i>	μ	Vol. %	<i>f</i>	-
Alpha-bromonaphthalene			Iso-butyl alcohol		
11.1	348	0.33	26.7	565	0.33
12	427	.30	27.7	625	.27
13	568	.26	28.7	795	.21
14.3	835	.217	29.7	994	.15
15	1150	.19	30.9	1190	.10
15.8	1420	.165	Linseed oil		
16.7	1690	.13	29.2	596	.268
Acetylene tetrabromide			30	636	.24
12	530	.29	31.9	875	.165
13	646	.25	33.5	1063	.10
13.6	786	.22	35	1260	.08
14.3	1007	.187	Ethyl carbonate		
15	1325	.15	25	167	.31
15.8	1590	.112	26.7	225	.25
16.3	1790	.10	27.7	289	.22
Iso-amyl alcohol			28.7	398	.20
28.7	556	.25			
29.6	616	.20			
30.3	765	.172			
30.8	864	.15			
31.5	967	.11			
32.1	1100	.09			
Alpha-chloronaphthalene					
13	410	.31			
14.3	530	.270			
15	625	.25			
15.4	716	.23			
15.8	935	.22			
16.7	1159	.19			
17.5	1525	.165			

ments. He further correlated these results with the plastic characteristics of corresponding mixtures. In the present work the plasticities of different concentrations of the three solids ZnS, ZnO, and carbon in linseed oil were measured. The yield value-concentration curves and the mobility-

concentration curves are shown in Figures 3, 4, and 5, and Figures 6, 7, and 8, respectively.

With the solids ZnS and ZnO the yield value-concentration curves seem to indicate that linseed oil has a rather high adhesion against these solids. That is, the curves fall in the same group with the alcohol curves. This, perhaps, should be expected since the formation of zinc soap in these

TABLE XI

THE RELATION BETWEEN THE VOLUMES PER CENT OF A SOLID IN A LIQUID AND THE TWO PROPERTIES, YIELD VALUE AND MOBILITY

<i>Carbon</i>					
Vol. %	<i>f</i>	μ	Vol. %	<i>f</i>	μ
Acetylene tetrabromide			Alpha-bromonaphthalene		
32.5	556	0.63	32.5	358	0.75
33.9	670	.53	33.9	420	.67
35.0	874	.43	35	516	.61
36.4	1265	.322	36.4	715	.53
37.2	1540	.245	38.1	1040	.43
38.1	1730	.18	40	1360	.322
38.5	1840	.142	Iso-butyl alcohol		
Alpha-chloronaphthalene			25.3	318	.51
32.5	420	.67	26.7	397	.43
33.9	516	.60	28.6	567	.32
34.8	621	.54	30.1	745	.23
36.4	865	.45	31.8	1014	.15
38.2	1200	.35	Linseed oil		
39.8	1500	.255	28.7	746	.73
Iso-amyl alcohol			29.5	825	.66
26.3	358	.43	30.9	965	.54
27.8	408	.315	32.4	1120	.42
29.4	527	.22	34.1	1290	.247
30.7	645	.142			
31.7	781	.10			
Ethyl carbonate					
26.7	258	.45			
28.6	347	.36			
30.8	466	.26			
32.3	596	.202			
33.9	781	.16			

systems is quite probable. Such soaps would tend to decrease the interfacial tension existing between the solid and the liquid phases.

The yield value-concentration curve of carbon with linseed oil seems to indicate that this system belongs to Group III. This is somewhat surprising as it indicates that linseed oil has an intermediate degree of wetting for carbon.

It would seem that a study of the plasticity of a given pigment with pure liquids would be a valuable preliminary step in determining the properties of a paint in which the pigment is to be used. By measuring the plasticity of the paste the general group into which the paste or paint falls could be determined. That is, one might predict whether a high, low, or intermediate force of attraction would exist between the pigment and a specified vehicle. With this information it seems probable that properties of practical importance may be more accurately predicted.

Summary

For convenience in the plastometric study of solid-liquid systems, the systems used were divided into three groups, namely: Group I, systems in which a high degree of adhesion exists between solid and liquid; Group II, systems in which a low degree of adhesion exists between solid and liquid; Group III, systems in which an intermediate degree of adhesion exists between solid and liquid.

The general results obtained and the conclusions drawn are as follows:

Group I.—Results: The experimental results show that for equal volumes per cent of solid, polar or non-polar, the paste formed with that liquid giving the *highest degree of adhesion* against the solid had the highest yield value, the lowest mobility, and the lowest concentration representing zero mobility.

Conclusions: (1) An adsorbed film of strongly oriented liquid molecules is firmly held by each solid particle. (2) Orientation of liquid molecules extends some distance into the liquid medium. (3) The plastic characteristics of such a system are due to resistance to deorientation offered by the oriented liquid molecules. (4) The yield value is relatively high and the mobility relatively low in a system in which the forces of attraction between solid and liquid are high.

Group II.—Results: The results show that for equal volumes per cent of a polar solid, the paste formed with that liquid giving the *lowest degree of adhesion* against the solid had the highest yield value, the lowest mobility and the lowest concentration representing zero mobility.

Conclusions: (1) The low force of attraction existing between the solid and the liquid leads to flocculation or grouping of the solid particles into clusters. (2) The plastic characteristics of such a system are largely dependent upon the friction between the solid particles. (3) The yield value is relatively high and the mobility relatively low in a system in which the forces of attraction between solid and liquid are low.

Group III.—Results: For equal volumes per cent of solid in two liquids,

the paste formed with that liquid giving the higher degree of adhesion against the solid has the lower yield value and the higher mobility.

Conclusions: The plastic characteristics of such a system are dependent upon a combination of influences, namely: the orientation of liquid molecules resulting from the force of attraction solid *vs.* liquid; the friction between the solid particles resulting from flocculation; and the fluidity of the liquid medium. It is impossible to definitely determine the predominating influence in this case. It is impossible, likewise, to determine with certainty the relation between the plastic characteristics of the pastes and the degree of wetting of the solid by the liquid.

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